Supplementary Information

D-A reaction between polyDVB-80 and TCNE

PolyDVB-80 microspheres (0.200 g) were suspended in toluene (20 mL) in a two-necked, round-bottomed flask (50 mL) fitted with a reflux condenser. TCNE (0.770 g, 6.00 mmol) was dissolved in the suspension. The flask was sealed with a rubber septum and the mixture was sparged with nitrogen. The flask was placed in an oil bath set at 30 ^{o}C and mixed using an overhead stirrer for 24 hours under a nitrogen atmosphere. The product was collected *via* vacuum filtration on a 0.45 μm nylon membrane filter, washed with toluene and dried overnight *in vacuo* (40 ^{o}C, ~ 0.01 bar). The product was isolated as a fine, brown powder (0.207 g). FTIR $\tilde{\nu}_{max}$/cm^{-1}: 3033 (aromatic C-H str.), 2931 (aliphatic C-H str.), 2174 (nitrile C≡N str.), 1614 (aromatic C=C str.), 1521 (aromatic C=C str.), 1454 (aliphatic C-H bend), 992 (vinyl C-H def.), 909 (1,2,4-trisubstituted aromatic out-of-plane C-H def.), 838 (1,4-disubstituted aromatic out-of-plane C-H def.), 798 (1,3-disubstituted aromatic out-of-plane C-H def.), 715 (1,3-disubstituted aromatic C-H def.). Elemental microanalysis (found, %): C, 86.2; H, 7.3; N, 2.2; TCNE loading level ~ 0.4 mmol/g.

Synthesis of Non-Porous PolyDVB-55 Core Microspheres

ACN (200 mL) and DVB-55 (3.699 g, 2% v/v relative to solvent) were added to a Nalgene bottle (500 mL). The solution of monomer in ACN was then ultrasonicated for 10 minutes to remove dissolved O_2. AIBN (0.156 g, 2 mol% relative to the number of polymerisable double bonds) was then dissolved in the monomer solution and the solution sparged with N_2 for 10 minutes to ensure complete removal of O_2. The bottle was then sealed under nitrogen with a screw-cap and placed on a Stovall low-profile roller housed inside a Stuart Scientific temperature-controlled incubator. The bottle was rolled slowly about its long axis at rate of approximately 10 rpm, and the temperature of the incubator was ramped from ambient temperature to 60 °C over a period of approximately 2 hours. Once the temperature reached 60 °C, it was held at this temperature for a further 22 hours. It was observed that particles began to phase separate around 8 hours after the start of the polymerisation. By the end of the polymerisation period, the crude product was in the form of a milky white suspension of polymer particles. The microspheres were isolated *via* vacuum filtration on a 0.45 μm nylon membrane filter. The microspheres were washed twice with ACN (2 x 20 mL) and then dried overnight in a vacuum oven to constant mass (40 °C, ~0.01 bar) to give the final product as a free-flowing, white powder (20% yield). FTIR $\tilde{\nu}_{max}/cm^{-1}$: 3036 (aromatic C-H str.), 2938 (aliphatic C-H str.), 1605 (aromatic C=C str.), 1520 (aromatic C=C str.), 1455 (aliphatic C-H def.), 996 (alkene out of plane C-H def.), 905 (alkene out of plane C-H def.), 830 (1,4-disubstituted aromatic out of plane CH def.), 799 (1,3-disubstituted aromatic out of plane C-H def.), 711 (1,3-disubstituted aromatic out of plane C-H def.). Elemental microanalysis (found, %): C, 90.7; H, 8.2; N, 0.6. ImageJ analysis of SEM micrograph: average particle diameter = 2.8 μm, CV = 4% (monodisperse). Nitrogen sorption analysis: SSA = 6 m^2/g.

Synthesis of Porous PolyDVB-55@PolyDVB-80 Core-Shell Microspheres

Non-porous polyDVB-55 core microspheres (0.5 g), ACN (75 mL) and toluene (25 mL) were added to a Nalgene bottle (250 mL). DVB-80 (1.514 g) was added to the bottle and the mixture then ultrasonicated for 10 minutes to remove dissolved O_2. AIBN (0.068 g, 0.42 mmol, 2 mol % relative to the number of polymerisable double bonds) was then added and the mixture sparged with N_2 for 10 minutes to ensure complete removal of O_2. The bottle was then sealed under nitrogen with a screw-cap and placed on a Stovall low-profile roller housed inside a Stuart Scientific temperature-controlled incubator. The bottle was

rolled slowly about its long axis at rate of approximately 10 rpm, and the temperature of the incubator was ramped from ambient temperature to 60 °C over a period of approximately 2 hours. Once the temperature reached 60 °C, it was held at this temperature for a further 46 hours. By the end of the polymerisation period, the crude product had retained the form of a milky white suspension of polymer particles. The microspheres were isolated *via* vacuum filtration on a 0.45 μm nylon membrane filter. The microspheres were washed twice with ACN (2 x 20 mL) on the filter and then dried over a period of 48 hours in a vacuum oven to constant mass (40 °C, ~0.01 bar) to give the final product as a free-flowing, white powder (1.100 g, 39%). FTIR $\bar{\nu}_{max}/cm^{-1}$: 3050 (aliphatic C-H str.), 1606 (aromatic C=C str.), 1518 (aromatic C=C str.), 1451 (aliphatic C-H def.), 994 (alkene out of plane C-H def.), 906 (alkene out of plane C-H def.), 838 (1,4-disubstituted aromatic out of plane C-H def.), 799 (1,3-disubstituted aromatic out of plane C-H def.), 711 (1,3-disubstituted aromatic out of plane C-H def.). Elemental microanalysis (found, %): C, 90.6; H, 7.9; N, 0.6. ImageJ analysis of SEM micrograph: average particle diameter = 6.4 μm, CV = 17% (polydisperse). Nitrogen sorption analysis: SSA = 452 m^2/g.

D-A reaction between Porous PolyDVB-55@PolyDVB-80 Core-Shell Microspheres and MA

MA (1.18 g, 12 mmol) was dissolved in toluene (40 mL) and added to a three-necked, round-bottomed flask fitted with a condenser and an overhead stirrer. Porous PolyDVB-55@PolyDVB-80 Core-Shell Microspheres (0.4004 g) were added to the flask and the mixture sparged with N_2 for 15 minutes. A rubber septum was then attached to the flask and a N_2 balloon was attached. The mixture was then refluxed for 48 hours. After cooling, the microspheres were isolated *via* vacuum filtration on a 0.45 μm nylon membrane filter, washed twice on the filter with toluene (2 x 20 mL), followed by acetone (10 mL), and dried *in vacuo* to a constant mass (40 °C, ~0.01 bar) to give the final product as a free-flowing off-white/orange powder (0.448 g). FTIR $\bar{\nu}_{max}/cm^{-1}$: 3042 (aromatic C-H str.), 2931 (aliphatic C-H str.), 1792 (anhydride C=O str.), 1606 (aromatic C=C str.), 1517 (aromatic C=C str.), 1451 (aliphatic C-H def.), 1070 (anhydride C-O str.), 999 (alkene out of plane C-H def.), 905 (alkene out of plane C-H def.), 831 (1,4-disubstituted aromatic out of plane C-H def.), 804 (1,3-disubstituted aromatic out of plane C-H def.), 711 (1,3-disubstituted aromatic out of plane C-H def.). Elemental microanalysis (found, %): C, 81.2; H, 7.1; N, 0.6; O (by difference), 11.0; anhydride loading level = 2.3 mmol/g.

Chromatographic conditions:

A Luna Omega Polar C_{18} 100 (150 x 3.0 mm, 5 µm particle size) equipped with a 3 mm precolumn (Phenomenex, Torrance, CA, United States) was selected as chromatographic column. The injection volume was set at 20 µL, the flow rate was 0.4 mL/min and the column oven temperature was 30 ºC. The solvents for the mobile phase in LC-DAD were ultrapure water adjusted to pH 3 with HCl (solvent A) and ACN (solvent B). When working with LC-HRMS, solvent A was MS grade water with 0.1 % of HCOOH. The gradient program started with 5% of B, increasing the %B to 60% within 6 min., then increasing the %B to 100% within 22 min., where it was held for 3 min.. 1 min. was used to return to the initial conditions, which were then maintained for 3 min.

When working with LC-DAD, two different wavelengths were used to quantify the analytes: 230 nm was used for ATE, MTO, DIC and BEZ and 210 nm was used for TRI, VEN, PRO, VAL and CLO. When working with LC-HRMS, two windows were used for quantification. The first one was used for basic analytes using positive ionisation mode, from the beginning to min. 13. The ions used for quantification and confirmation are detailed in Table S1. The conditions were: 40 AU (arbitrary units) for sheath gas flow rate, 15 AU for auxiliary gas flow rate, 5 AU for sweep gas flow rate, 4 kV for spray voltage, 45 V for capillary voltage, 65 V for tube lens voltage and 22 V for skimmer voltage. The second window was used to quantify the acidic analytes using negative ionisation mode, from min. 13 to the end. The conditions for this window were 40 AU for sheath gas flow rate, 15 AU for auxiliary gas flow rate, 5 AU for sweep gas flow rate, 4 kV for spray voltage, -25 V for capillary voltage, -60 V for tube lens voltage and -22 V for skimmer voltage. In both ionisation modes, the capillary temperature was set at 330 ºC and the heater temperature at 350 ºC. Each window had two alternative scan events with a range from 50 to 450 m/z. The first event consisted of a full scan at 50,000 FWHM (Full Width Half Maximum) with an injection time of 250 ms, meanwhile the second scan consisted of a fragmentation scan at 10,000 FWHM with an injection time of 50 ms and a collision voltage of 20 eV in both windows. In LC-HRMS, instrumental calibration curves ($R^2 > 0.995$) were obtained through weighted calibration regression for the compounds: the lower limit was 0.05 µg/L for TRI, MTO and PRO, 0.1 µg/L for ATE, VEN, CLO, BEZ and VAL, 0.25 µg/L for DIC and 2.5 µg/L for FEN. The upper limit was 500 µg/L in all cases.

Validation of the analytical method

To evaluate the efficiency of the extraction in LC-HRMS, the apparent recoveries (%R_{app}) were obtained as the ratio between the concentration obtained after SPE (subtracting the blank concentration) and the theoretical concentration.

The matrix effect (%ME) was obtained by spiking a non-spiked sample after SPE and comparing the concentration obtained (subtracting the blank concentration) to the theoretical concentration using the following formula %ME = (C_{exp}/C_{the} x 100) – 100, where "C_{exp}" represents the concentration obtained by spiking a non-spiked sample after SPE, subtracting the blank signal, and "C_{the}" represents the theoretical concentration. A negative value indicates MS signal suppression whilst a positive value indicates MS signal enhancement.

Accuracy was evaluated as the relative recovery, calculated as the percentage of the mean experimental concentration (n=3) and the spiked concentration. Method detection limits (MDL) and method quantification limits (MQL) were estimated by applying the preconcentration factor and the apparent recoveries to the instrumental limits. The instrumental detection limit was the concentration that presented a signal-to-noise ratio higher than 3 and one of the fragment ions had a signal higher than 10^3. The instrumental quantification limit was the lower point of the calibration curves.

Repeatability was obtained as the intra-day %RSD (relative standard deviation) (n=4) by analysing samples spiked at the same concentration on the same day. The reproducibility between days was obtained as the inter-day %RSD (n=4) by analysing samples spiked at the same concentration on different days.

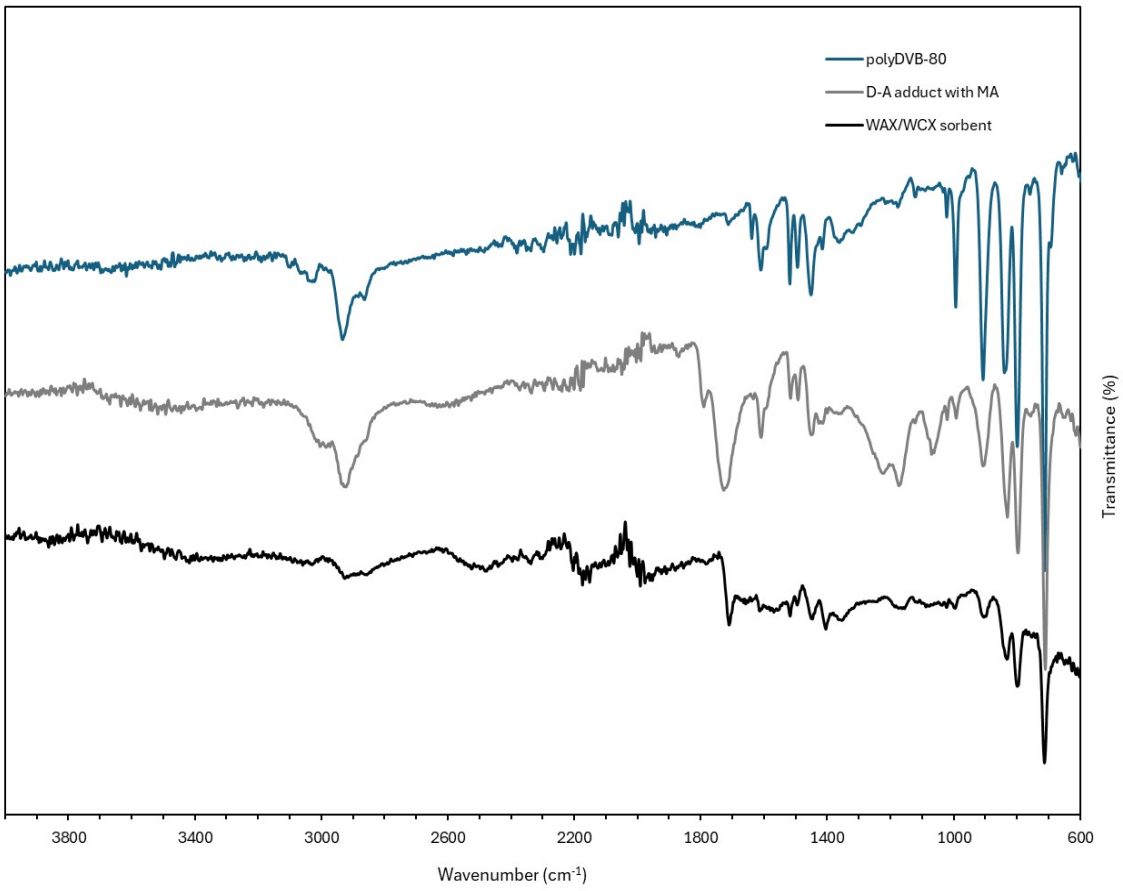

Figure S1.- FTIR spectra of polyDVB-80 microspheres (upper), the D-A adduct with maleic anhydride (MA) (middle) and the WAX/WCX sorbent formed upon ring-opening of the polymer-bound anhydride groups with ethylenediamine (EDA) (lower).

Table S1.- Protonated and deprotonated ions and fragment ions for the analytes.

	Compound	pK_a	$[M+H]^+$ (basic) and $[M-H]^-$ (acidic)	Fragment ion	Ratio
Basic	ATE	9.6	267.17020	190.08649	0.078
				145.06514	0.032
	TRI	7.1	291.14517	245.10388	0.067
				261.09866	0.050
	MTO	9.7	268.19061	116.10733	0.092
				191.10712	0.034
	VEN	10.1	278.21133	260.20111	0.022
				58.06614	0.271
	PRO	9.4	260.16418	116.10773	0.124
				183.08057	0.065
Acidic	CLO	3.2	213.03151	126.99430	0.553
				85.02819	0.126
	BEZ	3.8	360.10059	274.06412	0.607
				154.00548	0.024
	VAL	3.6	434.21912	350.16254	0.179
				179.08580	0.144
	FEN	4.5	241.08667	93.03340	0.945
				211.07599	0.324
	DIC	4.1	294.00919	250.01923	0.551
				250.01923	0.318

Table S2.- Method detection limits (MDL) and method quantification limits (MQL).

		River water		Effluent wastewater		Influent wastewater	
		MDL (ng/L)	MQL (ng/L)	MDL (ng/L)	MQL (ng/L)	MDL (ng/L)	MQL (ng/L)
Basic	ATE	0.2	1	0.7	2	2	6
	TRI	0.2	1	0.4	1	1	4
	MTO	0.3	1	0.4	1	2	5
	VEN	0.6	2	0.6	2	2	6
	PRO	0.2	1	0.3	1	1	3
Acidic	CLO	0.6	2	1	3	2	5
	BEZ	0.5	2	1	3	2	7
	VAL	1	3	1	4	2	6
	FEN	16	47	22	67	73	217
	DIC	2	6	3	9	8	23